491a Modeling Propane Aromatization on Hzsm-5 and Ga/Hzsm-5

Gowri Krishnamurthy, Aditya Bhan, Shuo-Huan Hsu, Yogesh Joshi, W. N. Delgass, J. M. Caruthers, G. E. Blau, K. T. Thomson, and Venkat Venkatasubramanian

This work addresses the development of a robust microkinetic model that describes the Aromatization of Propane over ZSM-5-based zeolites.

The conversion of light alkanes such as propane to aromatics and hydrogen is an industrially significant challenge for the creation of value-added products. ZSM-5, presenting a unique set of characteristics such as high surface area, well-defined porosity at a favorable size, high thermal stability, intrinsic acidity and high resistance to deactivation, serves as a valuable catalyst system for the problem. While the catalyst design variables include Si/Al ratio and gallium content in HZSM-5, in this work we report on the effect of gallium addition to HZSM-5, a method known to enhance the dehydrocyclization ability of the catalyst.

HZSM-5 catalysts obtained from ExxonMobil were characterized by XRD, BET, ^{29}Si and ^{27}Al MAS NMR and elemental analyses. The catalyst was thereby established as a crystalline material with a well defined porosity, negligible extra-framework Al species and Si/Al ratio of 16. The aromatization of propane over this catalyst was described by 311 elementary steps, including the activation of alkanes via the carbonium ion chemistry, hydride transfer, dehydrogenation, olefin adsorption / desorption, oligomerization, ß-scission and cyclization. The reactions were grouped into families based on the nature of the reactants, products and transition states. Quantitative modeling was performed using the Reaction Modeling Suite (RMS) that consists of modeling tools, such as a compiler to generate the kinetic equations, a differential algebraic equation generator and solver, a parameter estimation package and a statistical analyzer. The model parameterized in terms of 25 rate and equilibrium constants was observed to fit data at different temperature conditions, and the parameter estimates were found to compare well with literature values.

The addition of gallium to HZSM-5 was performed by the incipient wetness impregnation technique while the dispersion of gallium ions in the framework was accomplished by pre-treatment in Hydrogen at 530^{o}C. XRD confirmed the crystalline nature of the catalyst while elemental analysis was used to obtain accurate Ga exchange ratios. FTIR spectroscopy, performed after gallium introduction, indicated a steady decline in the strength of the 3610 cm^{-1} band with increase in Ga content, thereby suggesting that gallium sites compensate for a fraction of the Bronsted acid sites. A kinetic model with 18 parameters was postulated with this in mind. The 25 parameters of the non-exchanged proton sites were assumed to remain fixed, while the 18 new parameters for the gallium sites, mainly attributed to dehydrogenation activity, were fit to data at 10% Ga/Al, producing fairly good predictions. Interestingly, we also observed that the propane conversion as well as selectivity to aromatics goes though a maximum with the Ga/Al ratio, appearing to maximize at about 0.5. Our experimental observations thus point towards a synergistic mechanism between the proton and gallium sites. The mechanistic implications of models of this synergism, obtained by fitting the data over the full Ga composition range, will be discussed.